

Enhancement of Thermal Conductivity due to Spinons in the One-Dimensional Spin System SrCuO_2

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Abstract. We have measured the thermal conductivity along the c -axis parallel to the spin-chains, κ_c , of the one-dimensional antiferromagnetic spin system SrCuO_2 , using as-grown and O_2 -annealed single-crystals grown from raw materials with 99.9 % (3N) and 99.99 % (4N) purity. The value of κ_c around 50 K, where large contribution of the thermal conductivity due to spinons, κ_{spinon} , is observed, is markedly enhanced by both the increase of the purity of raw materials and the O_2 -annealing. Therefore, the increase of κ_c implies that κ_{spinon} is enhanced due to the decrease of spin defects caused by impurities in raw materials and by oxygen defects. The mean free path of spinons is as large as about 24000 Å at low temperatures in the O_2 -annealed single-crystal grown from raw materials with 4N purity.

1. Introduction

Recently, high thermal conductivity due to magnetic excitations in low-dimensional quantum spin systems has attracted great interest. For one-dimensional (1D) antiferromagnetic (AF) integrable Heisenberg systems with the spin quantum number $S = 1/2$, some theoretical calculations have suggested that the thermal conduction due to magnetic excitations, called spinons, tends to be ballistic, leading to large values of thermal conductivity due to spinons, κ_{spinon} [1, 2, 3]. Actually, large values of κ_{spinon} have been observed in the $S = 1/2$ 1D AF system Sr_2CuO_3 [4, 5] and SrCuO_2 [5]. Our recent work has proved that the thermal conduction due to spinons in Sr_2CuO_3 is ballistic at low temperatures [6]. In this study, the mean free path of spinons, l_{spinon} , of $\text{Sr}_2\text{Cu}_{1-x}\text{Pd}_x\text{O}_3$, where Cu^{2+} ions with $S = 1/2$ are partially replaced by nonmagnetic Pd^{2+} ions, has been found to be comparable with the length between spin defects estimated from the magnetic susceptibility measurements at low temperatures. This means that the spinons carry heat between spin defects without being scattered. In other words, there is a possibility of the enhancement of κ_{spinon} if the number of spin defects decreases in 1D AF systems.

So far, the highest value of κ_{spinon} among 1D AF systems has been obtained in SrCuO_2 [5] with zigzag spin-chains formed from two CuO chains combined with each other by sharing their edges of CuO_4 squares. In SrCuO_2 , the exchange interaction between the nearest Cu spins with the 180° Cu-O-Cu bond, J , and that between the diagonal Cu spins with the nearly 90° Cu-O-Cu bond, J' , have been estimated to be ~ 2000 K from magnetic susceptibility measurements [7] and to be as ferromagnetic as ~ -200 K from the theoretical calculation [8],

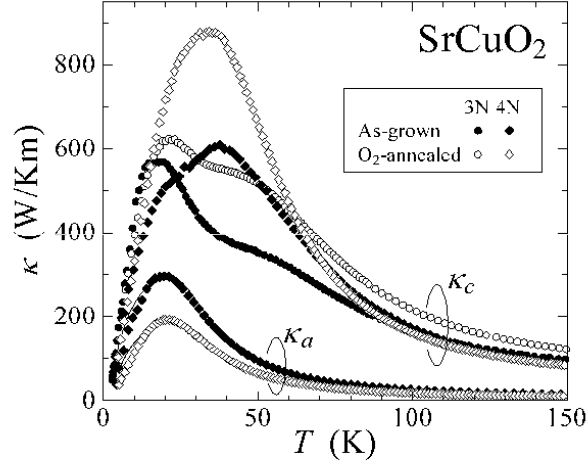


Figure 1. Temperature dependence of the thermal conductivity along the c -axis parallel to spin-chains, κ_c , and along the a -axis perpendicular to spin-chains, κ_a , for as-grown and O_2 -annealed single-crystals of $SrCuO_2$ grown from raw materials with 3N and 4N purity. Solid lines are fitting results of κ_{phonon} in κ_a .

respectively. Therefore, the zigzag spin-chain in $SrCuO_2$ can be regarded as two independent 1D AF spin-chains, but these are weakly coupled via J' with frustration [9].

Spin defects in $SrCuO_2$ appear on account of the vanishment of spins on Cu^{2+} ions, that is caused by substitution of nonmagnetic impurities for Cu and hole/electron doping. A spin-chain in $SrCuO_2$ is disconnected due to defects of oxygens in the Cu-O-Cu bonds also. Therefore, long spin-chains maybe prepared in $SrCuO_2$ by the single-crystal growth using raw materials with high purity and by the control of the oxygen content. Accordingly, in order to enhance κ_{spinon} in $SrCuO_2$, we have grown the single crystals using raw materials with 99.9 % (3N) and 99.99 % (4N) purity, and annealed those in O_2 atmosphere and measured the thermal conductivity.

2. Experimental

Single crystals of $SrCuO_2$ were grown by the traveling-solvent floating-zone (TSFZ) method. Polycrystalline feed rods for the TSFZ growth were prepared from $SrCO_3$ and CuO powder with 99.9 % (3N) and 99.99 % (4N) purity. It has been found from the iodine titration that as-grown single-crystals had oxygen defects. Therefore, as-grown single-crystals were annealed in O_2 gas flow at 870 °C for 48 h although it has been reported by Motoyama *et al.* [7] that spin defects are decreased by Ar-annealing. Thermal conductivity measurements were carried out by the conventional steady-state method.

3. Results and Discussion

Figure 1 shows the temperature dependence of the thermal conductivity along the c -axis parallel to spin-chains, κ_c , and along the a -axis perpendicular to spin-chains, κ_a , for the as-grown and O_2 -annealed single-crystals of $SrCuO_2$ grown from raw materials with 3N and 4N purity. In the as-grown 3N sample, the behavior of κ_c , which exhibits a peak around 20 K and a shoulder around 50 K, is similar to that reported by Sologubenko *et al.* [5]. The peak is due to the peak of the thermal conductivity due to phonons, κ_{phonon} , and the shoulder is due to the peak of κ_{spinon} . In the as-grown 4N sample, κ_c exhibits a small shoulder around 20 K and a peak around 40 K. Considering the peak temperature and the shoulder temperature, it is guessed that the shoulder and peak are due to peaks of κ_{phonon} and κ_{spinon} , respectively. Actually, κ_a in

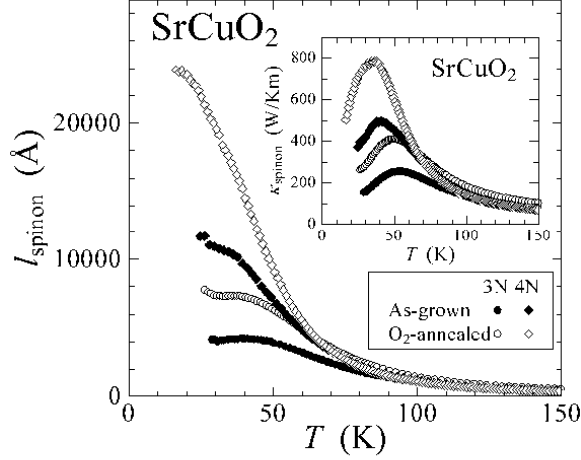


Figure 2. Temperature dependence of the mean free path of spinons, l_{spinon} , for as-grown and O_2 -annealed single-crystals of SrCuO_2 grown from raw materials with 3N and 4N purity. The inset shows the temperature dependence of the thermal conductivity due to spinons, κ_{spinon} .

the as-grown 4N sample exhibits only one peak due to κ_{phonon} around 20 K. Accordingly, it is concluded that the contribution of κ_{spinon} to κ_c is enhanced by the growth using raw materials with high purity.

It is found that κ_c in the 3N and 4N samples is enhanced by the O_2 -annealing also. In particular, the shoulder of the 3N sample and the peak of the 4N sample around 50 K, which are due to the peak of κ_{spinon} , are markedly enhanced by the O_2 -annealing. On the other hand, κ_a of the 4N samples is suppressed by the O_2 -annealing. These results mean that the number of spin defects decreases by the O_2 -annealing which is expected to connect Cu^{2+} ions separated by oxygen defects in the 180° Cu-O-Cu bond and also to remove excess electrons doped by oxygen defects. The suppression of κ_a by the O_2 -annealing may be caused by possible excess interstitial oxygens scattering phonons.

Here, we estimate the contribution of κ_{spinon} to κ_c in order to see the enhancement of κ_{spinon} clearly. At first, the estimate of κ_{phonon} is necessary. The temperature dependence of κ_{phonon} is usually given by the following equation based on the Debye model [10].

$$\kappa_{\text{phonon}} = \frac{k_B}{2\pi^2 v_{\text{phonon}}} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} \tau_{\text{phonon}} dx, \quad (1)$$

where $x = \hbar\omega/k_B T$, ω the phonon angular frequency, \hbar the Planck constant, k_B the Boltzmann constant and Θ_D the Debye temperature. The phonon velocity, v_{phonon} , is calculated as $v_{\text{phonon}} = \Theta_D (k_B/\hbar) (6\pi^2 n)^{-1/3}$, where n is the number density of atoms. The phonon scattering rate, $\tau_{\text{phonon}}^{-1}$, is given by the sum of scattering rates due to various scattering processes as follows,

$$\tau_{\text{phonon}}^{-1} = \frac{v_{\text{phonon}}}{L_b} + D\omega + A\omega^4 + B\omega^2 T \exp(-\frac{\Theta_D}{bT}), \quad (2)$$

where L_b , D , A , B and b are constants. These terms represent the phonon scattering by boundaries, by dislocations, by point defects and the phonon-phonon scattering in the umklapp process in turn. Here, Θ_D is put at 405.8 K from our specific heat measurements. The temperature dependence of κ_a of 4N as-grown and O_2 -annealed samples due to only κ_{phonon}

Table 1. Parameters used for the fit of the temperature dependence of the thermal conductivity along the c -axis, κ_c , with Eqs. (1) and (2).

	$L_b(10^{-3} \text{ m})$	$D(10^{-6})$	$A(10^{-43} \text{ s}^3)$	$B(10^{-18} \text{ sK}^{-1})$	b
3N as-grown	3.25	0.40	2.95	7.1	2.7
3N O ₂ -annealed	1.55	0.80	2.25	7.1	2.7
4N as-grown	2.11	2.40	8.00	7.1	2.7
4N O ₂ -annealed	2.24	6.50	8.50	7.1	2.7

is well fitting with Eqs. (1) and (2) as solid lines in Fig. 1. In this estimation, values of B and b for 4N as-grown and O₂-annealing samples are determined to be the same values, respectively. For the fit of κ_{phonon} to κ_c , values of B and b are put at the same values as those used for the fit to κ_a , respectively, because the phonon-phonon scattering in the umklapp process seems neither to be affected by the crystal direction, by the small change to the oxygen content, nor by the purity of raw materials. Adjusting three parameters of L_b , D and A , κ_{phonon} in κ_c is estimated. Then, κ_{spinon} is estimated by subtracting the fitting curve of κ_{phonon} from the data of κ_c , as shown in the inset of Fig. 2. The uncertain data of estimated κ_{spinon} at low temperatures are neglected. In this estimation, these three parameters are determined so that κ_{spinon} at low temperatures is proportional to temperature as theoretically expected. Values of the parameters used for the best fit to κ_c are listed in Table 1.

Next, we estimate l_{spinon} , using the following equation based on the Heisenberg model and the des Cloizeaux-Pearson mode [11],

$$l_{\text{spinon}} = \frac{3\hbar}{\pi N_s c k_B^2 T} \kappa_{\text{spinon}}, \quad (3)$$

where N_s is the number of spins and c is the lattice constant of the c -axis which is the same as the distance between the nearest neighboring spins in the spin-chain. It is found that l_{spinon} increases with decreasing temperature, as shown in Fig. 2. Value of l_{spinon} tend to be saturated at low temperatures. In this analysis, it is hard to estimate κ_{phonon} , κ_{spinon} and therefore l_{spinon} at low temperatures exactly. However, it is found that l_{spinon} is markedly extended by both the increase of the purity of raw materials and the O₂-annealing. This indicates that l_{spinon} is extended owing to the decrease of spin defects caused by impurities in raw materials and by oxygen defects. The maximum value of l_{spinon} in the O₂-annealed 4N sample is as large as $\sim 24000 \text{ \AA}$. The length between spin defects calculated from the purity of raw materials, L_{purity} , is 3918 \AA and 39180 \AA in 3N and 4N samples, respectively. In the 3N sample, the maximum of l_{spinon} is larger than the value of L_{purity} . It is possible that the spinons carry heat over the spin defects, because the spinons may be able to pass the spin defects through the weak interaction J' in the double spin-chains. This is different from the case in Sr₂CuO₃. There is another possibility that the quality of the raw materials is higher than just 99.9 %. In the 4N sample, on the other hand, the maximum of l_{spinon} is smaller than the value of L_{purity} . This indicates that κ_{spinon} is disturbed by spin defects due to oxygen defects. Therefore, it is expected that κ_{spinon} is enhanced by more suitable O₂-annealing.

4. Summary

We have measured the thermal conductivity of single crystals of SrCuO₂ grown from raw materials with 3N and 4N purity. The magnitude of κ_{spinon} has been found to become large by both the increase of the purity of raw materials and the O₂-annealing. Accordingly, we have succeeded in the enhancement of κ_{spinon} . This result indicates that l_{spinon} is able to be extended

by the removal of spin defects in $S = 1/2$ 1D AF systems where the thermal conduction due to spinons is ballistic, leading to the enhancement of κ_{spinon} .

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